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Dsc studies on the decomposition of chemical blowing agents based on citric acid and sodium bicarbonate

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ABSTRACT

This paper investigates the decomposition kinetics of citric acid, sodium bicarbonate and their combinations in masterbatches with low density polyethylene in view of their use in injection molding with simultaneous polymer foaming. The thermal decomposition was studied by isothermal and non-isothermal calorimetry to separate the various chemical events. A multi-step autocatalytic model was used to determine the kinetic parameters. Results show that for sodium bicarbonate compounds, the kinetics can be modeled by first-order equations while for citric acid compounds it shows two steps of decomposition due to reaction intermediates. The parameters obtained for the mono-component masterbatches can be used to model the kinetics of compounds containing a mix of sodium bicarbonate and citric acid with the same multi-step coupled equations. Experiments and modelisation show that the reaction in the masterbatch proceeds in well separated steps corresponding to each species. In particular, at high heating rates such as those encountered during melting in the injection molding machine, the citric acid decomposition occurs in a single step making the analysis of the kinetics and the modelling of the overall foaming process more simple.

1. Introduction

Blowing agents are increasingly used for the production of extruded or injection molded foamed items for cost saving, weight reduction, enhancement of thermal insulation effect and to improve surface texture. The foamed materials are generally used for plastic parts in domestic appliances, buildings, automotive industry, medical and food packaging. In recent years, industries have been looking for solution to cost-effective design and process, and for this purpose, the use of blowing agents provides a suitable solution. Physical blowing agents (PBAs) are injected into the process as liquid or gases whereas chemical blowing agents (CBAs) decompose to generate gases such as carbon dioxide under processing conditions at elevated temperatures in molten polymer. However, the foaming reaction of blowing agent in the complex thermal conditions of the various processes can be complex [1,2] and temperature control is critical to obtain proper foaming and production of gases. Firstly, the range of the temperature decomposition of chemical blowing agents must be close to that of the melting temperature of the polymer resin to avoid premature or incomplete decomposition. Secondly, strong temperature gradients can be generated during the melting. Finally, for proper dispersion in the hosting polymer and easier handling, the CBAs are used in the form of concentrated masterbatches in polymer. Environmental concerns and food industry have also driven the use of non toxic or hazardous compounds.

Citric acid (CA) and sodium bicarbonate (SB) meet the non-toxicity requirements and they become widely used in injection molding of polyolefins because the temperature range of the decomposition reactions match the processing temperature. Fig. 1 show the main reactions [3–5].

Sodium bicarbonate decomposes at low temperature over a broad temperature range (100–180 °C) in a first-order reaction or a 2/3 order reaction [6–8]. According to Wu and Shih [9] differences of reaction order between the authors [10,11] may be essentially due to particle size. Citric acid decomposes over a broad temperature range, 160–270 °C. Barbooti et al. [12] showed that citric acid first melts at 153 °C and then decomposes at higher temperatures by dehydration to give aconitic acid after a conversion of one third of the blowing agent, and finally methyl maleic anhydride (citraconic acid anhydride) by decarboxylation. The overall reaction order was found to be close to 2. DSC studies of Wyrzykowski et al. [4] confirmed the intermediates of the reaction, cis-aconitic acid and trans-aconitic acid ($C_6H_6O_6$), and the dehydration and decarboxylation reactions that further yield trans-aconitic anhydride ($C_6H_4O_5$) or itaconic anhydride ($C_5H_4O_3$). Blends of

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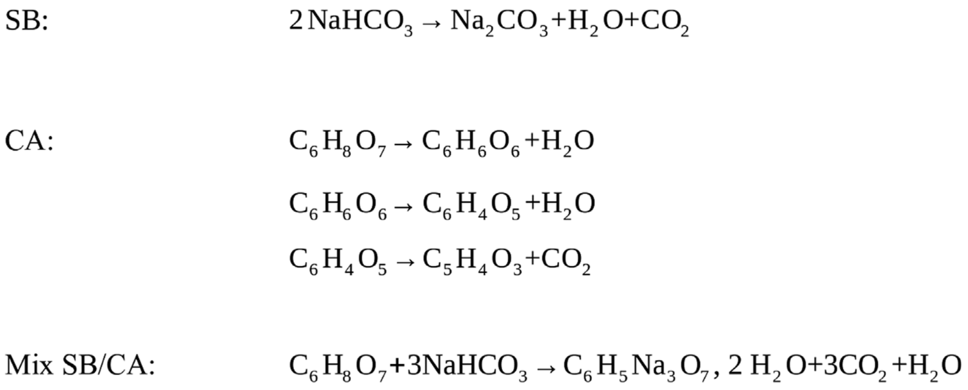

SB:
$$2\,NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2$$

CA:
$$C_6H_8O_7 \rightarrow C_6H_6O_6 + H_2O$$
$$C_6H_6O_6 \rightarrow C_6H_4O_5 + H_2O$$
$$C_6H_4O_5 \rightarrow C_5H_4O_3 + CO_2$$

Mix SB/CA:
$$C_6H_8O_7 + 3NaHCO_3 \rightarrow C_6H_5Na_3O_7,\ 2\,H_2O + 3CO_2 + H_2O$$

Fig. 1. Decomposition schemes of sodium bicarbonate, citric acid and their mix.

citric acid and sodium bicarbonate in various proportions enable to obtain foams having medium cell sizes. The reaction begins at 160 °C and is completed at about 210 °C [13] and gives water vapor, carbon dioxide and a solid residue (sodium citrate dihydrate). Hydrocerol® (Clariant) chemical blowing agents are typical mixtures of citric acid and sodium bicarbonate generally blended in stochioemetric proportions. The decomposition generates various gaz, liquids and solid products among which CO_2, H_2O, Na_2CO_3, $C_6H_6O_6$, $C_6H_4O_5$ and $C_5H_4O_3$. Behravesh et al. demonstrated that the decomposition behavior of these compounds is sensitive to the heating rate [14]. Soares and Nachtigall studied such blowing agent mixed within PP/wood flour composites and used masterbatches in polyethylene [15]. The reaction kinetics of mix of sodium bicarbonate and citric acid were investigated by Dixon et al. [16] in PP in crosslinked polyolefins using both isothermal and dynamic conditions. Recent works have shown the urge for a good knowledge of the kinetics of decomposition in order to get a better control of foaming during extrusion or injection-molding of polyolefins [17–20].

The aim of the present work is to address the decomposition kinetics of citric acid, sodium bicarbonate or of the mixture of both incorporated in masterbatches of polyolefins to get information on the kinetics to model and understand the foaming process in core-back injection molding [18]. This is done by performing isothermal and dynamic experiments in differential scanning calorimetry and by using a two steps autocatalytic model. This model enables to get a set of kinetic parameters to describe the conversion of citric acid or sodium bicarbonate masterbatches in isothermal or non isothermal experiments. The same model was used for the calculation of the conversion in a masterbatch with equal weight of the components.

2. Materials and methods

2.1. Materials

The experiments were carried out on three chemical blowing agents based on masterbatches of sodium bicarbonate (SB), citric acid (CA) and a mix (MX) of both in equal weight fractions, in an olefinic matrix. These products are distributed by Clariant under the trade names Hydrocerol® ITP 848, Hydrocerol® ITP 828 and Hydrocerol® ITP 818. These three chemical blowing agents are conventionally used with thermoplastic polyolefins. Their characteristics are given in Table 1. The infra-red spectroscopy confirms that the polymer matrix of the masterbatches is LDPE (double peaks at 2800–3000 cm^{-1}) and also confirms the composition of the active compounds showing peaks of sodium bicarbonate at 3300–3500 cm^{-1} (OH) and at 1600 cm^{-1} (CO), and peaks of citric acid at 3300 cm^{-1} (OH), at 1750 cm^{-1} (CO) and at 1400–1550 cm^{-1} (CH).

Table 1
Characteristics of the masterbatches containing various chemical blowing agents.

Reference in this study	SB	CA	MX
Active compound	Sodium bicarbonate	Citric acid	Blend of citric acid and sodium bicarbonate
Active compound (wt-%)	70	70	65
Temperature of start of decomposition (°C)	160	200	160
Polymer Matrix	LDPE	LDPE	LDPE

2.2. Methods

Differential Scanning Calorimetry (DSC) measurements were carried out with a Q10 TA instrument under nitrogen flow. The mass of the samples was 4 ± 0.5 mg in all cases. All the measurements were obtained from the first scan. The isotherms were run in a temperature range covering the temperature range of decomposition of each compound, from 130 to 155 °C for SB and from 190 to 210 °C for CA with a 5 °C increment and from 140 to 220 °C for MX with a 10 °C increment. For all isothermal analyses, fast heating at 50 °C/min was applied to reach the targeted temperature. Then the sample was held at this temperature during 60 min for SB and CA, or 10 min for MX. The dynamic experiments were carried out over a temperature range from 40 to 230 °C with a heating rate of 2.5, 5, 10, 15 and 20 °C/min. The CBAs fully react in the first scan and a second scan shows only the melting of the matrix at 110 °C that was already visible in the first scan. Heating rates between 2.5–20 °C/min were applied in the measurements. The heating rate 20 °C/min may look high for heating polymers since the heat conductivity of polymers is low and thermal gradients may might appear in the samples. However, this high heating rate remains of interest from the practical point of view because it is close to what is used in the injection molding conditions especially during the melting of the polymer in the barrel of the plasticating unit.

Thermogravimetric analysis (TGA) experiments were carried out on a Mettler Toledo TGA/DSC 1. The samples with mass of 5 ± 0.5 mg were heated at 10 °C/min from 40 to 600 °C under nitrogen flow (80 ml/min).

2.3. Numerical methods

Calculations were performed with the open source software for numerical computation Scilab. Marquard-Levenberg non linear optimization routine (*lsqrsolve*) was used to fit the kinetic parameters in the kinetic equations using the full set of experimental data. Systems of ordinary differential equations were solved by the (*ode)* solver in Scilab. Solutions of low order equations were used as starting values for increasing order equations. For multi-step models, each step was first